

Chapter 18

EFFECTIVENESS OF HALON ALTERNATIVES IN SUPPRESSING DYNAMIC COMBUSTION PROCESSES

by

**W.L. Grosshandler, C. Presser
Building and Fire Research Laboratory and
Chemical Science and Technology Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899
and
G. Gmurczyk
Science Applications Interactional Corp.
555 Quince Orchard Road
Gaithersburg, MD 20878**

American Chemical Society Halon Replacements - Technology and Science Symposium, August 21-25, 1994, Washington, DC. Chapter 18. Sponsored by the Division of Environmental Chemistry, Inc. 208th National Meeting. ACS Symposium Series 611. Andrzej W. Miziolek, and Wing Tsang, Editors. American Chemical Society, Washington, DC. 1995.

NOTE: This paper is a contribution of the National Institute of Standards and Technology and is not subject to copyright.

Chapter 18

Effectiveness of Halon Alternatives in Suppressing Dynamic Combustion Processes

W. L. Grossharter¹, G. Gmurczyk^{1,3}, and C. Presser²

¹Building and Fire Research Laboratory, Fire Science Division, and

²Chemical Science and Technology Laboratory, Chemical Kinetics
and Thermodynamics Division, National Institute of Standards
and Technology, Gaithersburg, MD 20899-0001

C_3F_8 is shown to require the least storage volume among twelve fluorocarbons for suppressing a quasi-detonation. CF_3I performs the best of the gaseous suppressants evaluated in a spray burner. Two experimental facilities are described as part of an effort to identify suitable replacements for CF_3Br in aircraft applications. A turbulent spray burner simulates the hazard associated with a ruptured fuel line in an engine nacelle or dry bay. A deflagration/detonation tube evaluates the ability of a gaseous agent to attenuate the pressure build-up and Mach number of a quasi-detonation.

Halon 1301 (CF_3Br) is no longer produced in the U.S., forcing the manufacturers, owners, and users of aircraft to search for an alternative fire suppressing agent (1). A research program was established at NIST to focus specifically on engine nacelle and dry bay protection. The nacelle is the portion of the airframe which surrounds the jet engine. The engine system certification process requires that enough agent be available to maintain a minimum concentration (6% by volume for halon 1301) throughout the nacelle for a 0.5 s time interval to ensure that the fire will be extinguished and not relight. Dry bays refer to normally closed spaces adjacent to flammable liquid storage areas that are vulnerable to anti-aircraft fire. The entire suppression sequence occurs in under 100 ms in the dry bay.

The experiments described here are two of dozens that were developed (2) to identify the best chemicals for subsequent full-scale aircraft fire extinguishment evaluation at Wright-Patterson Air Force Base. The discriminating factors elucidated by the test protocols were lumped into four categories: (i) agent dispersion characteristics, (ii) required storage volume, (iii) environmental factors, and (iv) operational issues. The results presented in this paper are limited to the flame suppression studies which directly impact the estimate of agent storage volume required on board the aircraft. However, the dispersion character of the different agents in cold-flow

³Current address: Science Applications Interactional Corporation, 555 Quince Orchard Road, Suite 500, Gaithersburg, MD 20878

experiments varied more extensively than the amount of the agent required for flame suppression. The agent leaves the storage vessel, pressurized with N_2 at about 4 MPa, and immediately flashes or breaks into droplets, evaporates, and mixes with ambient air. The timing of this process is critical, and can render an agent which requires less mass to extinguish a laboratory flame ineffective in suppressing an actual aircraft fire. The reader is referred to the thorough discussion by Pitts et al. (2, Section 3) for details on how the agents were screened based upon the dispersion process.

Four different flame suppression facilities were designed with the objective of examining the flame extinction properties of the agents over the whole range of conditions likely to be encountered by aircraft in flight: (i) an opposed-flow diffusion flame (OFDF) burner, (ii) a cup burner, (iii) a turbulent spray burner, and (iv) a detonation/deflagration tube. The results of the turbulent spray and deflagration/detonation suppression experiments are summarized here. The OFDF and cup burner results are discussed in a companion chapter in this Series (3). Readers should refer to the Special Publication by NIST for additional details on the suppression experiments (2, Section 4).

Fluorocarbons (FCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and CF_3I were examined and compared to the performance of N_2 and CF_3Br . The behavior of sodium bicarbonate powder was studied in the spray burner only. All of the agents are listed with their physical properties in Table I. Air was the oxidizer, and the fuels included ethene, a jet fuel (JP-8), and a hydraulic fluid (MIL-H-83282C).

Turbulent Spray Flames

A fuel spray provides a unique opportunity for supporting a fire. Small droplets quickly evaporate and the momentum from the spray efficiently entrains the air necessary for combustion. A ruptured high pressure fuel, lubricant or hydraulic fluid line can supply a steady flow of fuel for a fire stabilized behind obstacles in the engine nacelle, or create a cloud of droplets from a punctured fuel tank adjacent to a dry bay. Extinguishment of the burning spray will occur when the critical level of agent is mixed with the air that gets entrained into the reaction zone. The process is affected by the velocity of the air flow, the rate that the agent is added to the air, the system temperature, and the agent and fuel concentrations and properties.

Experimental Facility. The spray burner facility consisted of an air delivery system, a fuel delivery system, an agent injection system, and a combustor. Figure 1 shows a cross-sectional view through the combustion zone. Air at atmospheric pressure co-flowed around the fuel tube within a 0.5 m long, 50 mm diameter stainless steel pipe. A Pyrex tube extension, 75 mm long, was used to observe the flame under confined conditions. The fuel was injected along the centerline through a pressure-jet nozzle, flush with the open end of the surrounding passage. The flame was stabilized on a 35 mm diameter steel disk attached to the nozzle body. The nominal air velocity across the burner was 33 m/s. The fuel (JP-8 or hydraulic fluid) was delivered at a rate of about 0.5 ml/s when the gauge pressure was 687 kPa.

The gaseous agents were injected impulsively into the air 0.54 m upstream of the nozzle using a computer controlled solenoid valve. Uniform dispersion across the air stream was enhanced by injecting the gas in a radial direction into a reduced diameter

Table I. Physical properties of agents evaluated (2, Section 2)

Agent		Molec. Wt., g/mole	P _v @ 25 °C, MPa	T _{bp} @ 101 kPa, °C	Sat. Liq. Density @ 25 °C, kg/m ³
Designation	Formula				
nitrogen	N ₂	28	^a	-196	^a
halon 1301	CF ₃ Br	149	1.61	-57.8	1551
halon 13001	CF ₃ I	196	0.49	-22.0	2106
FC-116	C ₂ F ₆	138	^a	-78.2	^a
FC-218	C ₃ F ₈	188	0.88	-36.8	1321
FC-31-10	C ₄ F ₁₀	238	0.27	-2.0	1497
FC-318	cyc-C ₄ F ₈	200	0.31	-7.0	1499
HFC-125	C ₂ HF ₅	120	1.38	-48.6	1190
HFC-32/125	CH ₂ F ₂ /C ₂ HF ₅	67	1.67	-52.5	1040
HFC-134a	C ₂ H ₂ F ₄	102	0.67	-26.2	1209
HFC-227ea	C ₃ HF ₇	170	0.47	-16.4	1395
HFC-236fa	C ₃ H ₂ F ₆	152	0.27	-1.5	1356
HCFC-22	CHF ₂ Cl	87	1.05	-40.9	1192
HCFC-124	C ₂ HF ₄ Cl	137	0.38	-13.2	1357
sodium bi-carbonate	NaHCO ₃	84	^b	^b	^b

^a 25 °C is above critical temperature of compound^b solid powder, blended with silica

section of the air passage. Screens were placed downstream of the injection point to ensure complete mixing between the air and agent prior to encountering the flame zone. The amount of injected agent was controlled by varying the initial pressure and the time that the solenoid valve was open. The actual mass delivered was determined from the difference between the initial and final pressures in the storage vessel (5).

The gaseous injection system was modified to accommodate powders. The sodium bicarbonate was loaded into two nylon tees downstream of the computer-controlled solenoid valve. Straight-through ball valves isolated the powder from the burner to minimize back-flow and powder loss during loading. Compressed air stored in the agent vessel was used to propel the powder into the burner.

The independent parameters which were controlled in the spray burner facility were the air flow and temperature, the fuel flow and type, the agent composition, and the mode of injection (fixed time or fixed pressure). The particle size distribution and

the transport gas pressure were varied for the powdered NaHCO_3 . The dependent parameters in the experiments were the mass and the rate of injection required for suppression.

The protocol used to evaluate the gaseous agents incorporated a fixed injection interval of 75 ± 10 ms. The fuel spray was ignited and the air flow set to the desired level. The flame was allowed to burn for several minutes to ensure steady operation. If the air was at an elevated temperature, it was necessary to wait until the temperature at the burner stabilized. The agent storage vessel was evacuated and then flushed several times with the chemical under investigation. The pressure in the vessel was adjusted with the solenoid valve closed to a value which was expected to be insufficient to extinguish the flame. The computer control/data acquisition was initiated and the response of the flame to the injection process was observed. If the flame was not extinguished, the pressure in the agent vessel was increased and the experiment was repeated under the same operating conditions. Eventually a pressure was found which was sufficient to suppress the flame. This procedure was normally repeated four times for each agent. Additional details on the facility and its operation have been given previously (2, Section 4; 4; 5).

Experimental Results. The mass fraction of agent required to extinguish the flame, β , is defined by the average mass flow of the agent divided by the sum of the agent and air flows. The mass of agent added to the flame and the actual time interval of agent injection were determined from pressure-time traces (5).

The injection time interval had an effect on the minimum amount of nitrogen required to extinguish the flame. The closed-circles plotted in Figure 2 illustrate this effect. For these experiments, the pressure was fixed and the injection time interval was gradually increased until extinction occurred. The minimum mass of nitrogen was about 0.32 g, for a set injection period of 23 ms. Reducing the set time to 6 ms had no impact on the amount of nitrogen required to quench the flame because of the finite time response of the solenoid valve. Injection times as long as 260 ms more than tripled the amount of N_2 required. A limit was reached at long time intervals where transient mass addition was insufficient to extinguish the flame.

Nitrogen was allowed to flow continuously in one experiment, with the rate increasing until the flame was extinguished. The mass fraction of N_2 required to suppress the flame was 0.11, and is indicated by the continuous flow arrow in Figure 2. This compares to a value of 0.28 found in a cup burner (3) with the same fuel/agent combination. Less nitrogen was required for extinguishment of the spray flame because of the greater turbulence levels and reduced time available for the combustion to occur. The solid triangles also plotted in the figure are values of β that correspond to the different injection time intervals. As the time is shortened, β increases, reaching a limiting value of about 0.28. For an agent that is to be used in a transient manner, the total mass must also be considered. This is distinct from the quasi-steady state measurements taken with the cup burner apparatus, for which β is a reasonable measure of performance for a total flooding agent.

Gaseous Agent Test Series. Extinguishment experiments were first performed using halon 1301 to establish a baseline. An average over five experiments led to a CF_3Br mass of $0.44 \pm .04$ g and a β of 0.15 required for flame suppression. The

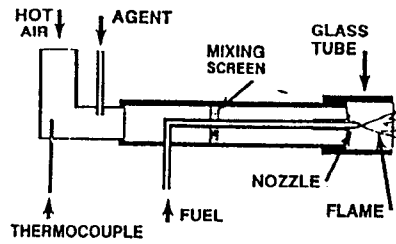


Figure 1. Cross-section of combustion zone of spray burner facility.

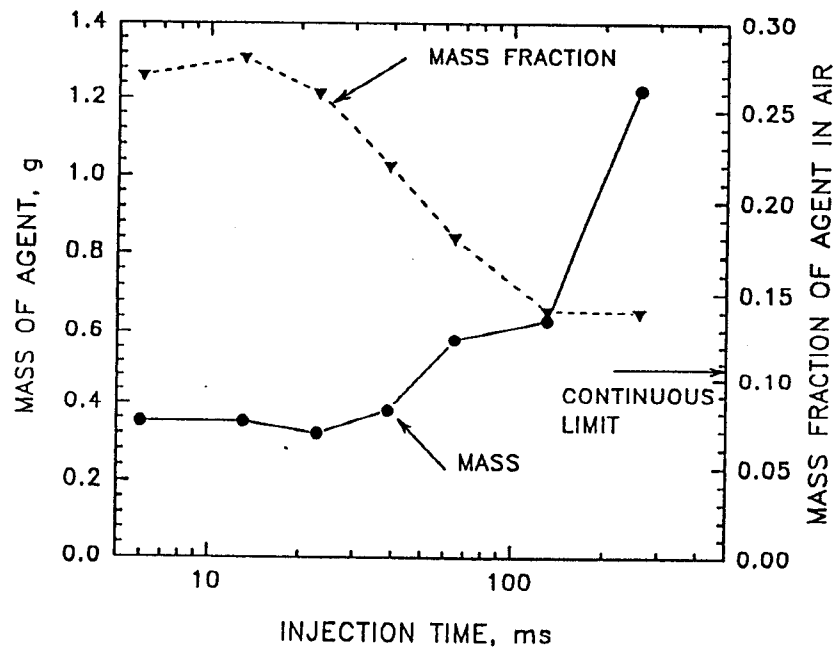


Figure 2. Effect of injection time on the total mass and mass fraction of N_2 required to extinguish JP-8 spray flame.

results of the ambient temperature air/JP-8 flame suppression experiments for all of the gaseous chemicals examined are summarized in Table II. The CF_3I required the least mass (0.54 g) and a mass fraction of 0.16, close to that of CF_3Br . Nitrogen was only slightly less effective. HCFC-22 was the next most effective, requiring 0.65 g for suppression; FC-31-10 required the most (1.00 g) material and the highest mass fraction (0.27) to extinguish the flame.

The air was preheated to 150 °C and the experiments were repeated with all of the gaseous agents except for CF_3I (4). The increase in temperature affected the flame stability in several ways. First, since the mass flow of air remained fixed, the average velocity across the air duct increased about 50% due to the drop in density. The JP-8 in the line was also warmed as it flowed through the heated air annulus. The higher temperatures and lower fuel density required the fuel pressure to be increased to deliver the same amount. However, even at a maximum fuel line pressure of 1.03 MPa-g, the mass of fuel was only 90% of the ambient temperature condition, resulting in a slightly leaner flame. The increase in air velocity and decrease in equivalence ratio somewhat destabilized the flame; but this was counteracted by the increase in enthalpy of the reactants due to the higher initial temperature.

As seen in Table II, increasing the temperature, on average, increased the amount of agent required to suppress the JP-8 spray flame by 0.04 g. The halon 1301 remained the most effective, but in relative and absolute terms, required the largest increase in mass of all the chemicals investigated. The nitrogen remained better than the other halogenated compounds, and FC-31-10 remained the least effective. It can be speculated that the relatively poorer behavior of the halon 1301 is attributable to two possible reasons: the decreased residence time of the agent in the flame, and the increased temperature near the flame front. Both physical effects could reduce the number of bromine atom/hydrogen radical interactions.

A flame could not be stabilized using MIL-H-83282C hydraulic fluid and ambient temperature air. By increasing the air temperature to 120 °C and by operating closer to stoichiometric conditions (the fuel volume flow was increased by 27% over the JP-8 flame), sufficient stability was maintained. A bluish appearance of the hydraulic fluid spray flame suggested that less soot was being formed.

There was little difference in the amount of halogenated agent necessary to suppress the hydraulic fluid spray when compared to the JP-8 flames. (See Table II, and note that neither FC-31-10 nor CF_3I were tested with the hydraulic fluid.) In particular, the amount of halon 1301 was identical to the unheated jet fuel experiments. About 10% more FC-318 was used to suppress the hydraulic fluid. By contrast, 28% less nitrogen extinguished the hydraulic fluid flame. An explanation for this unique behavior is not available.

Sodium Bicarbonate Powder Experiments. There was a definite particle size effect on the efficiency of the powder as a fire suppression agent. Table II summarizes the results. The smallest particle size powder was 2 1/2 times more effective in its fire suppression capability than the large particle size powder. There was no significant difference in performance created by changing injection pressure of the smallest particles. On the other hand, increasing the injection pressure increased the effectiveness of the large particle size by more than 20%. The enhancement in performance can be explained by the improved mixing of the powder into the flame as the injection

Table II. Amount of agent required to suppress turbulent spray flame (2, Sect. 4)

Agent	JP-8, $T_{air}=20\text{ }^{\circ}\text{C}$		JP-8, $T_{air}=150\text{ }^{\circ}\text{C}$		Hydraulic Fluid, $T_{air}=120\text{ }^{\circ}\text{C}$	
	mass, g	β	mass, g	β	mass, g	β
halon 1301	0.44	0.15	0.53	0.19	0.44	0.16
CF ₃ I	0.54	0.16	*	*	*	*
nitrogen	0.58	0.18	0.63	0.19	0.42	0.16
HCFC-22	0.65	0.20	0.70	0.23	0.70	0.24
HFC-125	0.73	0.22	0.77	0.24	0.78	0.26
HCFC-124	0.74	0.22	0.75	0.22	0.70	0.23
FC-116	0.75	0.22	0.74	0.23	0.73	0.23
HFC-134a	0.76	0.24	0.78	0.23	0.79	0.26
HFC-236fa	0.78	0.23	0.84	0.25	0.78	0.24
HFC-227ea	0.80	0.24	0.81	0.24	0.82	0.26
HFC-32/125	0.81	0.24	0.89	0.26	0.82	0.25
FC-218	0.89	0.24	0.87	0.25	0.86	0.28
FC-318	0.97	0.25	0.99	0.26	1.08	0.30
FC-31-10	1.00	0.27	1.02	0.25	*	*
NaHCO ₃ , < 10 μm	0.20	0.08	*	*	*	*
NaHCO ₃ , > 50 μm	0.52	0.18	*	*	*	*

* not measured

pressure increases and as the particle size decreases. The β values indicate a very effective agent for small particles, and a rather average performing agent for the large particle size (2, Section 4).

High speed movies of injection of the 0-10 μm particles showed what appears to have been a uniform powder cloud passing through the burner in about 80 ms. This compared to an injection interval equal to 75 ms based upon the recorded air pressure in the storage vessel. The photographs also showed that flame extinction happened within the first 50 ms from the time the powder reached the flame. This time was independent of injection pressure, and was close to the 40 ms estimated from high speed photographs of HCFC-22 suppressing a similar flame.

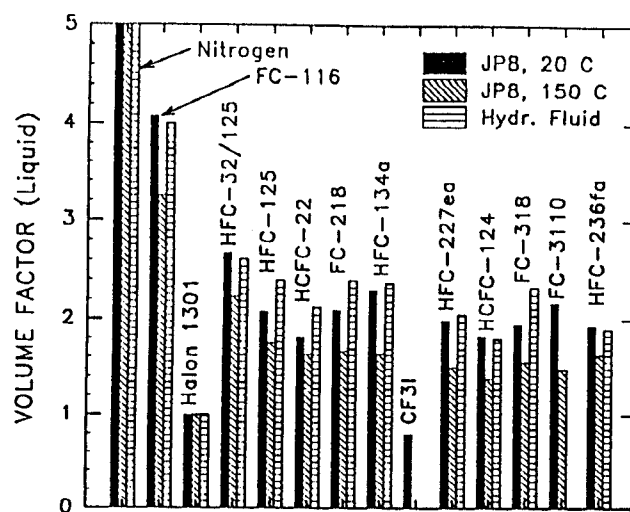
Discussion of Spray Flame Experiments. If the agents are ranked according to the mass required to inhibit the flame, the order does not change by more than plus or minus one position for the three series of experiments. The exception is HFC-125, which drops two positions in both of the high temperature tests. Expressing the results in terms of the flame suppression number (FSN) is a convenient way to compare the performance of the different agents in the three series of experiments. The FSN is defined as the mass fraction of agent relative to the mass fraction of halon 1301 used to suppress the equivalent flame. For the ambient temperature JP-8 flame, the FSN ranges from about 1.4 to 2.1 for the various agents, which is about 25% less than the FSNs measured in the cup burner (3).

Minimizing the storage volume on board the aircraft is as critical as minimizing the mass of agent. The density of the saturated liquid agent at ambient temperature provides a logical conversion from the mass required to the storage volume because the saturated liquid condition at ambient temperature is close to the condition maintained when the fire extinguishing bottle is filled (assuming negligible solubility of the pressurizing gas). The volume factor, VF, is defined as the volume of the agent in the cylinder required for flame suppression normalized by the equivalent volume of halon 1301. Figure 3 compares the performance of the different agents in this fashion, using (i) ambient temperature air and JP-8 (open bars), (ii) 150 °C air and JP-8 (cross-hatch bars), and (iii) 120 °C air and hydraulic fluid (solid bars). Nitrogen requires a storage volume 36 times that of halon 1301, and is off the scale in Figure 3 because it does not liquify under typical bottle conditions. The FC-116 also rates poorly on a volume basis because its critical temperature is less than the ambient. In the figure, the density of FC-116 was calculated at 25 °C and 4.1 MPa, a typical bottle pressure. The remainder of the agents have storage volume factors between 1.5 and 2.5, depending on the agent, fuel and temperature. Of these, the HFC-32/125 mixture has the highest volume factor, and HCFC-124, HFC-227ea and HCFC-22 have the lowest. The powdered agent was not compared on a volume basis since the volume of the system depends upon the pressurizing method as much as on the volume of the powder. The superior performance of the NaHCO₃ powder is evident, however, from the value of its FSN, which is less than 0.9 (2).

Conclusions from Turbulent Spray Burner Study. The turbulent spray burner has been found to be suitable for comparing the performance of gaseous and fine powder extinguishing agents in transient operation. The facility is not overly sensitive to the air or fuel flows, and the agent delivery system is able to control accurately the injection period between 20 and 910 ms.

The following conclusions are made regarding the ability of different agents to extinguish the spray flame:

- No statistically significant difference in agent performance was found between the room temperature JP-8 and hydraulic fluid flame testing, indicating little fuel effect.
- The majority of the agents require slightly more mass to extinguish the higher temperature JP-8 flame, indicating a small temperature effect. This trend is not completely unexpected since a higher temperature leads to more rapid fuel evaporation and greater flame stability. However, the temperature effect does not alter the ranking on agent performance, with the exception of HFC-125.



AGENTS (in increasing boiling point order)

Figure 3. Volume factor (VF) based upon liquid volume of agent relative to liquid volume of CF_3Br required to extinguish turbulent spray flame.

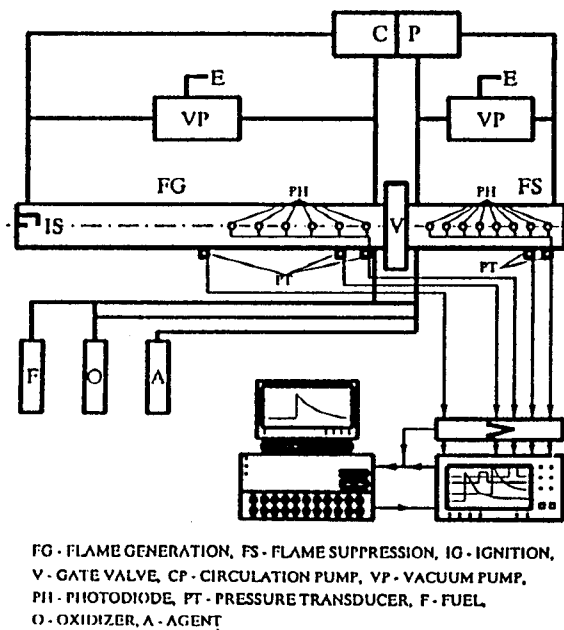


Figure 4. Schematic diagram showing major components of the deflagration/detonation tube facility.

- The FCs, HFCs and HCFCs all perform better in a turbulent spray burner relative to halon 1301 than is predicted from cup burner measurements. Generally speaking, almost twice as much mass and volume are needed to suppress the spray flame using the alternative agents when compared to halon.
- The amount of agent required for flame suppression decreases with increasing rate of agent injection.

Quasi-detonations

An anti-aircraft projectile entering a dry bay could lead to a situation in which a vaporizing fuel spray produces a combustible mixture which is then ignited by a glowing fragment. If the space were confined, the pressure would increase behind the reaction front, accelerating the flame. A transition to turbulence would likely occur as the flame encounters clutter in the dry bay. If the ventilation is insufficient to relieve the pressure build up, the possibility of a supersonic detonation would exist, leading to destructive over-pressures in the dry bay.

Supersonic combustion is distinct from the flames simulated in a spray burner. As a result, the effectiveness of an agent in preventing a detonation depends upon different chemical and physical mechanisms. A shock wave precedes the supersonic reaction zone. Obstructions in the flow promote intense mixing of the fresh reactants with the combustion products and cause the pressure waves to interact with the mixing region. Given enough distance, the flame can accelerate dramatically, increasing the temperature of the reaction zone behind the shock and further adding to the heat release rate. Depending upon the geometric details, the detonation wave can approach its theoretical Chapman-Jouguet velocity and accompanying high pressure ratio.

Deflagration/detonation Tube Experimental Facility. The effectiveness of a fire fighting agent in suppressing high speed, premixed combustion or a quasi-detonation can be rated by the extent to which it decelerates the propagating wave and simultaneously attenuates the hazardous shock which always precedes the combustion process. The traditional experiment in which the flame inhibitor is premixed with the fuel and air prior to ignition does not replicate the chemistry critical to the actual situation since in a dry bay the suppressing compound is injected after the combustion process has been initiated.

The two-section, deflagration/detonation tube shown in Figure 4 was designed to produce the desired environment for both the flame initiation and flame suppression regimes. The complexities and biases associated with the fluid dynamics of agent release were avoided by premixing the agent with the fuel and air in a portion of the tube distinct from where the flame is initiated. A repeatable, uninhibited turbulent flame was fully established in the driver section, the design of which was based directly upon the work of Peraldi et al., (6). In this study it was found that a 50 mm inner diameter tube with a blockage ratio of 0.43 could be used to create repeatable, high-speed flames and quasi-detonations within the first several meters of an 18 m tube. By varying the equivalence ratio of ethene/air mixtures from 0.5 to 2.1, they were able to produce flame velocities between about 600 and 1300 m/s.

The driver section used in the current project (labeled "FG" in Figure 4) was 5 m long and was equipped at the closed end with a spark plug ("IS"). This section was

filled with the combustible mixture of ethene and air. The gas handling system consisted of a vacuum pumping network ("VP" in figure); pressurized gas cylinders for the fuel ("F"), oxidizer ("O") and agent ("A"); and a dual circulating pump ("CP"). The ignition energy was delivered in a microexplosion of a tin droplet that short-circuited the tips of nichrome electrodes connected to an 80 V power supply. Spiral-shaped obstructions made of 6.4 mm stainless steel rods with a pitch equal to the inner diameter of the tube were inserted to produce an area blockage ratio of 44%. This ratio is similar to the value shown by Lee et al. (7) to promote a quasi-detonation in their facility.

The second section of the deflagration/detonation tube ("FS" in Figure 4) contained the gaseous agent along with the same fuel/air mixture used in the driver section. The diameter was the same and its length was 2.5 m. An identical spiral insert was used to maintain a high level of mixing. The two sections were separated from each other by a 50 mm inner diameter, stainless steel, high vacuum gate valve ("V"), which remained closed until just before ignition. Pressure transducers ("PT") and photodiodes ("PH") were located along the test section to monitor the strength and speed of the combustion wave. Their output was recorded on a multi-channel, digital storage oscilloscope.

Operating Procedure and Characterization. The deflagration/detonation tube was evacuated to 0.1 Pa before filling the driver and test sections separately with the desired mixtures. The fuel/air ratio and total pressure were held constant across the gate valve. The initial temperature was the ambient value. The oxidizer used in all experiments was breathing grade air. Ethene (99.5% volume purity) was chosen as the fuel because it had been demonstrated (7) that subsonic flames, quasi-detonations, and full detonations all could be obtained in a tube of this geometry simply by varying the stoichiometry.

About ten seconds prior to ignition, the gate valve was opened manually. After ignition, the flame propagated into the driver section and accelerated quickly. The flame/shock system, shown schematically in Figure 5, encountered the same combustible mixture plus agent as it passed through the gate valve and into the test section. Depending on the concentration of the agent, the flame was or was not extinguished and the pressure wave attenuated.

Mach number and pressure ratio were the two dependent parameters which were measured as a means to characterize the extent of flame suppression. The Mach number was based upon the time it took for the pressure wave to travel the distance between the two pressure transducers, normalized by the sonic velocity of the reactant gases in the test section. The pressure ratio was determined from the average amplitude of the first pressure pulse to be recorded by each transducer, normalized by the initial pressure. Consecutive pressure jumps occurred, indicating that localized explosions were present in the mixing region between the spirals. Individual runs were concluded before the shock wave reflected from the end plate and arrived back at the pressure transducers. The distance between the leading shock wave and the flame front was measured in some of the experiments from the time lag between the photodiode and pressure transducer response at the same location. The primary independent variables were agent type and concentration.

Characterization experiments were conducted with 100% nitrogen in the test

section, a 5% ethene-in-air mixture in the driver section (fuel/air equivalence ratio equal to 0.75), and the total pressure equal to 100 kPa. The incident shock wave velocity measured 2.2 m beyond the gate valve and 0.3 m from the end of the tube was 420 ± 8 m/s. The pressure ratio based upon the initial pressure rise was 2.5 ± 0.5 , and about 3.0 ± 1.0 based upon the peak increase. No significant changes in shock speed occurred for a partial pressure fraction (which is approximately equal to the mole fraction) of nitrogen in air greater than 40%. When no suppressing nitrogen was added to the test section the shock velocity attained a value of 1170 m/s. The pressure ratio based upon the initial rise, P_1/P_0 , increased dramatically at the same point as the velocity when the partial pressure of nitrogen was decreased, reaching a maximum of 18 when no nitrogen was added to the ethene/air mixture. The peak pressure ratio, which normally did not correspond to the initial pressure pulse, was around 30:1. The shock velocities and pressure ratios are presented in Figures 6 and 7 as a function of the partial pressure fraction of added N_2 in the test section for 100 kPa and two lower initial pressure conditions.

Stoichiometric and rich (equivalence ratio equal to 1.25) mixtures were ignited to determine the combustion wave parameters with no nitrogen added to the test section. The shock Mach number increased to 4.1 for stoichiometric and 4.5 for rich mixtures, and the corresponding pressure ratios were 26:1 and 35:1. With 100% N_2 in the test section the Mach number dropped to 1.3 and the pressure ratio to 3.5 when the mixture was stoichiometric.

The results of the preliminary parameter assessment led to an experimental protocol with wave speeds that were reproducible from run-to-run (to within about $\pm 2\%$). Pressures downstream of the shock wave had a higher variability ($\pm 20\%$) because of the complex shock structures created by interactions with the spiral rod inserts. More details can be found in (2, Section 4) and in the paper by Gmurczyk et al. (8).

Results and Analysis. Experiments using halon 1301 were studied and compared to an inerting agent like N_2 . Halon 1301 suppressed the flame at a partial pressure fraction of 10% to the same extent as if the test section had been completely filled with nitrogen. An unusual behavior occurred in the 100 kPa experiments when the concentration was between 2% and 3%. Both the Mach number and pressure ratio increased with the amount of CF_3Br , followed by the expected decrease for large concentrations. This reversal, while small, was greater than the uncertainty in the data.

Lean Mixtures. Attenuation of the shock speed and pressure increase by the agents was measured with the ethene/air equivalence ratio fixed at 0.75 (5.0% by volume C_2H_4), an initial absolute pressure of 100 kPa, and an initial temperature of 22 °C. It was found that the amplitude and speed of the pressure wave, and the speed of the trailing flame, were all strongly dependent on the agent type and concentration. The flame always followed the shock wave in such a way that both speeds were equal. However, when the amount of the agent in the mixture was increased, the distance between the shock and flame increased as well, up to around 100 mm as full suppression was approached. At the extinguishing concentration the radiation disappeared, which indicated the absence of the flame. In that situation the pressure wave amplitude was attenuated by a factor of eight and the wave speed by a factor of three, similar to the results for nitrogen.

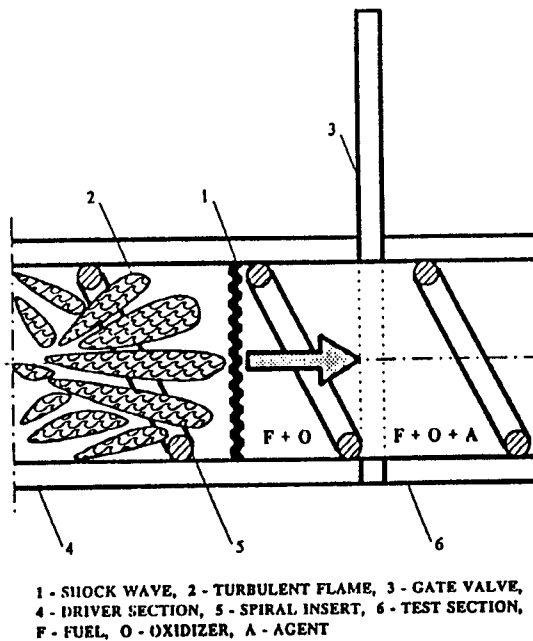


Figure 5. Rendering of high speed turbulent flame entering test section.

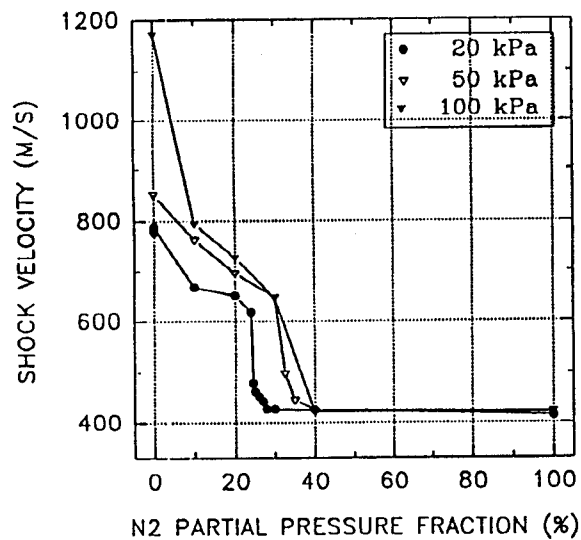


Figure 6. Effect of added nitrogen partial pressure and initial total pressure on the shock velocity in the deflagration/detonation tube.

The results for the FCs, HFCs and the HCFCs are compared in Figures 8 through 10. The pressure ratios at zero mass fraction represent the pure combustible mixture with no flame suppressing agent present. One can see that the agent mass fractions necessary for total extinguishment range from around 30% for the FCs to almost 50% for CHF_2Cl . At low concentrations the pressure ratios are higher for some agents than even the value for the pure combustible mixture. The FCs, as a class, were generally the best performers on both a partial pressure and mass fraction basis. In fact, FC-116 was superior to CF_3Br , and FC-318 was about equivalent. FC-218 and FC-31-10 slightly enhanced the pressure ratio in low concentration. This can be seen in Figure 8. FC-218 reduced the pressure ratio to less than 5:1 at a mass fraction of 0.29, which was better than with CF_3Br .

Adding hydrogen to the molecule had a significant effect on the performance of the HFCs, shown in Figure 9. The $\text{CH}_2\text{F}_2/\text{C}_2\text{HF}_6$ mixture produced peak pressures more than double the value for no suppressant. The Mach number was increased to its highest value of 4.1 when the mass fraction was 11%. It was not until the mass fraction exceeded 38% that the HFC-32/125 mixture became as effective as nitrogen in reducing the speed and pressure build-up of the shock wave. The two fluoropropanes, HFC-227ea and HFC-236fa produced the lowest pressure build-up of the HFCs and effectively reduced the shock speed.

The chlorine atom in the two HCFCs created an additional complexity because chlorine is a strong oxidizer. From Figure 10, one can see that HCFC-22 was the least effective on a mass basis of all of the agents in fully suppressing the combustion wave pressure ratio, requiring a mass fraction of over 50% in the test section. The maximum pressure ratio for HCFC-124 was 32:1 at a 23% mass fraction, which was exceeded only by HFC-125 and the HFC-32/125 mixture.

The one iodofluorocarbon tested was CF_3I . The Mach number and pressure build-up, shown in Figure 11, were reduced by about one half with partial pressure fractions in the test section of only 15 to 20%. None of the other chemicals, including CF_3Br , was able to accomplish this. Unfortunately, when the mass fraction was increased to 30%, the Mach number shot back up and the pressure ratio attained a value of 21:1, which was greater than when no CF_3I was present. This reversal, which was slight in the bromine-containing halon 1301, changed what at first appeared to be the most effective suppressing agent into one of the least effective agents. It is known that iodine atoms can cause a catalytic effect in some reactions by lowering the overall activation energy. At intermediate concentrations the possibility also exists that the iodine (and bromine) recombine, reducing their impact on the combustion process.

Stoichiometric Mixtures. To see if the relative performance of the agents was dependent upon the fuel/air ratio, a number of experiments were carried out under stoichiometric conditions. The equivalence ratio was based upon the amount of ethene in the mixture and was not adjusted to account for the contribution of the agent to the fuel or oxidizer pool. The initial pressure and temperature remained the same for the stoichiometric experiments: 100 kPa and 22 °C.

The Mach number and pressure ratio increased as the fuel/air mixture was changed from lean to stoichiometric. However, the relative behavior was not significantly altered for the FCs nor the CF_3I . That is, the pressure ratio vs. mass fraction curves were shifted upward about uniformly.

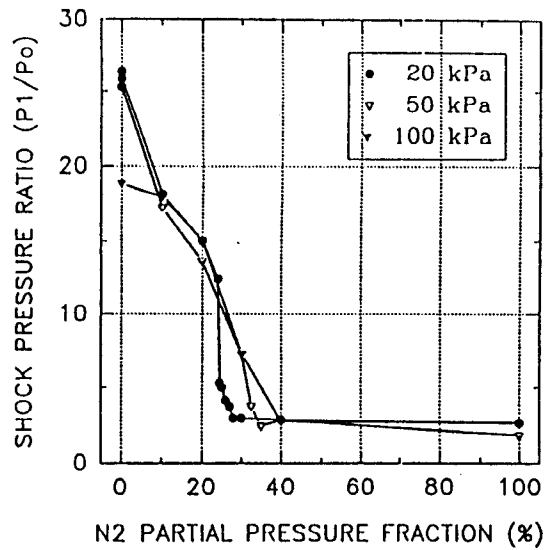


Figure 7. Effect of added nitrogen partial pressure and initial total pressure on the initial shock pressure ratio in the deflagration/detonation tube.

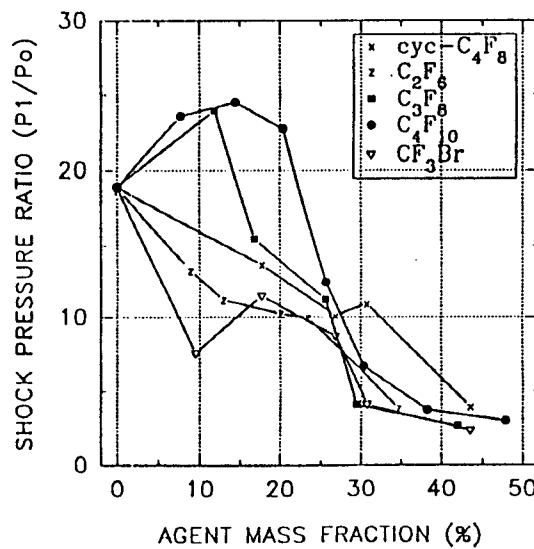


Figure 8. Reduction in pressure ratio as a function of FC mass fraction, compared to CF₃Br.

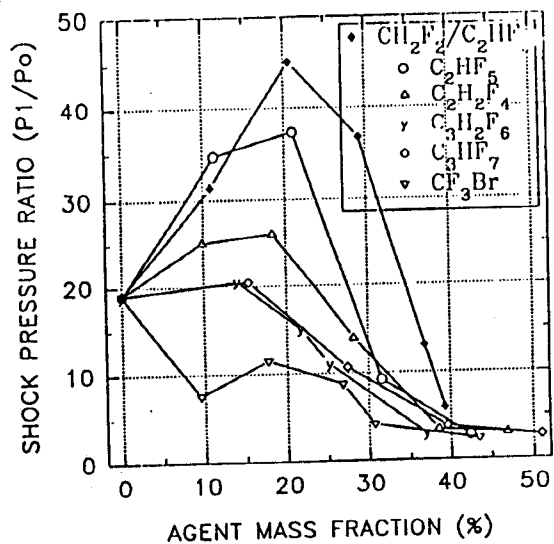


Figure 9. Reduction in pressure ratio as a function of HFC mass fraction, compared to CF_3Br .

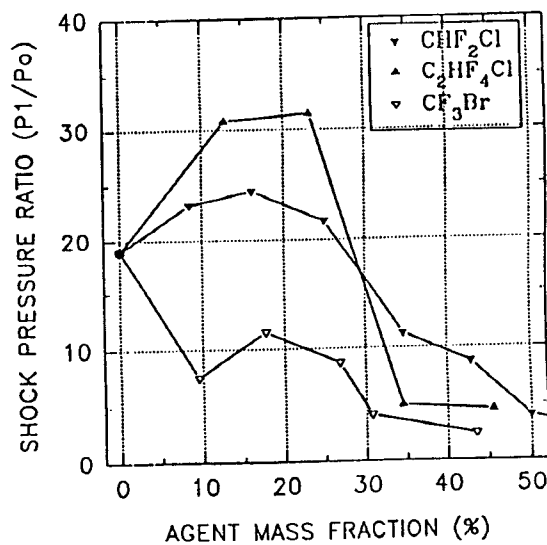


Figure 10. Reduction in pressure ratio as a function of HCFC mass fraction, compared to CF_3Br .

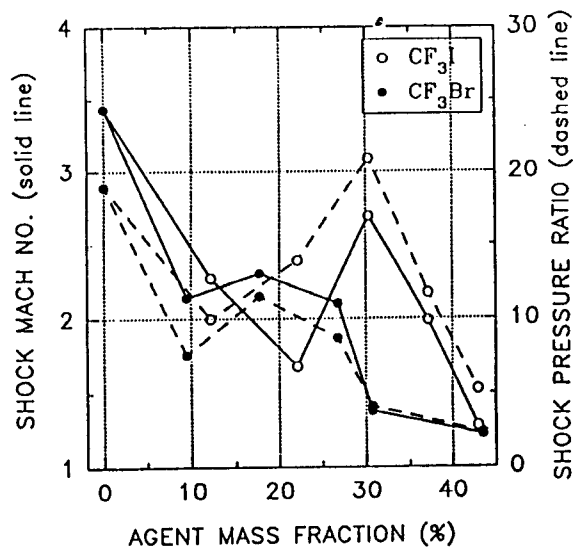


Figure 11. Reduction in shock wave Mach number and pressure ratio as a function of CF_3I mass fraction, compared to CF_3Br .

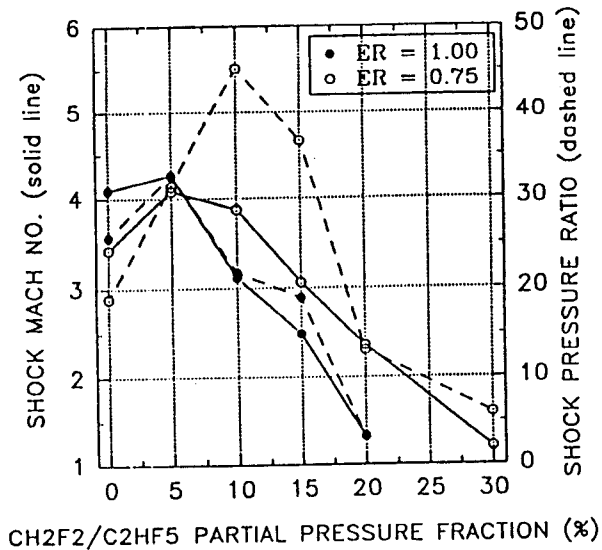


Figure 12. Effect of equivalence ratio on the reduction in shock Mach number and pressure ratio for HFC-32/125 mixture.

A distinctly different behavior occurred with the HFC-32/125 mixture, shown in Figure 12. The hydrogen atoms attached to the agent molecules had less of an enhancing effect under stoichiometric conditions ($ER = 1.0$). The over-pressure was greatly reduced when the equivalence ratio was increased, leading to a cross-over condition where both the Mach number and pressure ratio were reduced for the stoichiometric condition.

Ranking the Agents. The results that were gathered indicated the complexity of the suppression process in the deflagration/detonation tube. Because one does not know *a priori* the conditions in an actual dry bay fire zone, and because different initial conditions (i.e., pressure, temperature and fuel/air ratio) affect the amount of agent required for suppression to varying degrees, the following specific set of initial conditions was chosen at which all the agents were compared: 100 kPa, 22 °C, and 0.75 ethene/air equivalence ratio. The reduction in pressure ratio rather than the Mach number was chosen as the measure of suppression because of the direct impact of pressure on the structural integrity of the dry bay. The amount of halon 1301 required to reduce the pressure (i) to 10% and (ii) to one-half the maximum increase were used to normalize the results.

Figure 13 displays three different performance parameters calculated under these conditions: the volume factor (VF), the flame suppression number (FSN-mass) based upon the mass fraction, and the flame suppression number based upon the relative partial pressures (FSN-pp). While there were some reversals depending upon the basis of evaluation (i.e., 90% reduction FSN, 50% reduction FSN, or VF), Figure 13 (based upon 50% reduction) is representative of the relative behavior. FC-218 was clearly the best performer under the conditions tested, and the HFC-32/125 mixture and HCFC-22 were the worst. The FSN of FC-116 based upon a 50% reduction in pressure build-up was the lowest of all agents, even performing better than halon 1301. However, because hexafluoroethane does not condense at room temperature, its density is low, leading to a volume factor which is less desirable. On a mass basis nitrogen (not shown in figure) performed almost as well as halon 1301. It is also a gas at room temperature, though, and had a huge VF of 32. The CF_3I performed relatively well on a volume basis because of its high liquid density, but less well based upon the mass required.

Conclusions from the Deflagration/Detonation Study. It is necessary to emphasize that the experimental conditions in the deflagration/detonation tube differed significantly from those used in the turbulent spray flame burner. The main qualitative difference was the occurrence of a strong shock wave ahead of the flame. That wave influenced the gas dynamic, thermodynamic and chemical state of the pure combustible mixture in the driver section and the mixture containing an agent in the test section. Another feature was a high level of turbulence within the flame due to its high speed and the interactions with the spiral obstruction. The quantitative difference was a supersonic regime (relative to the undisturbed mixture) of flame/shock propagation and strong pressure changes (due to confinement and shock) during the process. Thus, the oxidizer, fuel and agent molecules were preconditioned prior to entering the flame zone.

It is concluded that suppression of highly dynamic flames can be effectively

- Sodium bicarbonate was the most effective suppressant of the turbulent spray flame, requiring less mass than halon 1301. The smaller size particles were more effective.
- Iodotrifluoromethane was more effective than halon 1301 in suppressing the spray burner flame, and was less effective in attenuating the shock speed and pressure in the deflagration/detonation apparatus.
- The gaseous agents required between 1 1/2 and 4 times the storage volume of halon 1301 to suppress the different flames.
- HCFC-124 was the best performer of the gaseous agents (other than CF₃I) in suppressing the turbulent spray flame, and FC-218 was judged the best for attenuating the shock speed and pressure in the deflagration/detonation tube.
- FC-116 was the poorest performer (on a liquid storage volume basis) of the agents evaluated in the spray flame suppression tests; the HFC-32/125 mixture was the second poorest performer in the spray flame, and led to the highest over-pressures in the lean deflagration/detonation tube study.

Acknowledgments

The authors wish to acknowledge the U.S. Air Force, Navy, Army and Federal Aviation Administration for funding the Agent Screening for Halon 1301 Aviation Replacement project. The program was directed by Michael Bennett at the Wright Patterson AFB, Flight Dynamics Laboratory, Vehicle Subsystems Division, Survivability Enhancement Branch. The contributions of Isaura Vázquez, Darren Lowe and William Rinkinen to the spray burner experiments are also gratefully acknowledged.

Literature Cited

1. Harrington, J.L. *NFPA J.* March/April 1993, pp 38-42.
2. *Evaluation of Alternative In-flight Fire Suppressants for Full-scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*; Grosshandler, W.L.; Gann, R.G.; Pitts, W.M., Eds.; NIST SP 861; National Institute of Standards and Technology: Gaithersburg, MD, April 1994.
3. Trees, D.; Seshadri, K.; Hamins, A. In *Halon Replacements: Technology and Science*; Miziolek, A.W.; Tsang, W., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1995.
4. Vázquez, I.; Grosshandler, W.; Rinkinen, W.; Glover, M.; Presser, C. In *Fourth Inter. Symp. on Fire Safety Science*; Kashiwagi, T., Ed.; IAFSS, USA, 1994.
5. Grosshandler, W.L.; Presser, C.; Lowe, D.; Rinkinen, W., "Assessing Halon Alternatives for Aircraft Engine Nacelle Fire Suppression," *J. Heat Transfer*, in press, 1995.
6. Peraldi, O.; Knystautas, R.; Lee, J.H. In *Twenty-first Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1986; pp 1629-1637.
7. Lee, J.H.; Knystautas, R.; Chan, C.K. In *Twentieth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1984; pp 1663-1672.
8. Gmurczyk, G.; Grosshandler, W.; Peltz, M.; Lowe, D. In *Chemical and Physical Processes in Combustion*; Eastern States Section of The Combustion Institute: Princeton, NJ, 1993; pp 487-490.

RECEIVED July 20, 1995